

DERWENT-ACC-NO: 2002-463460

DERWENT-WEEK: 200323

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TITLE: Fatty acid ester production for use as diesel  
fuel substitute, by concentrated sulfuric acid-  
catalyzed esterification of glycerol phase obtained as  
by-product in transesterification of fatty acid glycerides

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PATENT-ASSIGNEE: ENERGEA-UMWELTECHNOLOGIE GMBH[ENERN] , WIMMER  
T[WIMMI]

PRIORITY-DATA: 2000AT-001887 (November 8, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 0238529 A1	May 16, 2002	DE
AU 200213634 A	May 21, 2002	EN
AT 200001887 A	September 15, 2002	DE
AT 410443 B	March 15, 2003	DE

DESIGNATED-STATES: AE AG AL AM AU AZ BA BB BG BR BY BZ CA CH CN CO CR  
CU CZ DE  
DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR  
KZ LC LK  
LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI  
SK SL TJ  
TM TR TT TZ UA UG US UZ VN YU ZA ZW AT BE CH CY DE DK EA ES FI FR GB  
GH GM GR  
IE IT KE LS LU MC MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO
WO2002038529A1	N/A	2001WO-AT00348
November 7, 2001		
AT 200001887A	N/A	2000AT-001887
November 8, 2000		
AT 410443B	N/A	2000AT-001887
November 8, 2000		
AU 200213634A	Based on	2002AU-013634

November 7, 2001

INT-CL-CURRENT:

TYPE	IPC	DATE
CIPS	C07C67/03	20060101
CIPS	C07C67/08	20060101
CIPS	C10L1/02	20060101
CIPS	C11C3/00	20060101
CIPS	C11C3/04	20060101

ABSTRACTED-PUB-NO: WO 0238529 A1

BASIC-ABSTRACT:

NOVELTY - Production of fatty acid esters (I) of 1-4C alcohols (II) involves neutralizing glycerol phase (P1) obtained during transesterification of fatty acid glycerides with (II) and esterifying obtained mixture of fatty acids (III) and (I) using (II) where: neutralized (P1) is esterified using excess (II); mixture is separated into (I) phase (P2) and aqueous phase (P3) containing excess (II); (P2) is purified; (P3) is used to neutralize (P1).

DESCRIPTION - Production of fatty acid esters (I) of 1-4C alcohols (II) (specifically methanol) involves neutralization of the glycerol (heavy) phase (P1) obtained as a by-product in alkali-catalyzed transesterification of fatty acid glycerides with (II) and sulfuric acid-catalyzed esterification of the obtained mixture of free fatty acids (III) and (I) using (II), where:

(a) neutralized (P1) is esterified using excess (II) in presence of concentrated sulfuric acid and the reaction mixture is separated into a (I) phase (P2) and a phase (P3) containing excess (II), sulfuric acid and water of reaction;

(b) (P2) is purified by treatment with alkali metal (preferably potassium) hydroxide, washing with water and/or acid and evaporating excess (II); and

(c) (P3) is used for neutralization of further (P1), such that the neutralized mixture separates into a light phase containing (III), (I) and (II) and a heavy phase containing glycerol, excess (II) and alkali metal sulfate.

USE - (I) is used as a diesel fuel substitute (biodiesel) (claimed).

ADVANTAGE - Further (I), suitable for biodiesel use, is produced from the by-product phase (P1) formed in the production of (I) by transesterification of fatty acid triglycerides with (II). The (II) present in (P1) is also recovered for recycling, together with crude (60-90%) glycerol. If potassium hydroxide is used for neutralization, the sulfuric acid is converted into potassium sulfate suitable for use as agricultural fertilizer (rather than non-biodegradable waste products). Esterification (in presence of a relatively high sulfuric acid concentration) is carried out with low energy consumption at moderate temperatures, to give a degree of esterification of more than 95%. An economical and environmentally friendly overall process for producing biodiesel is thus provided.

#### EQUIVALENT-ABSTRACTS:

#### ORGANIC CHEMISTRY

Preferred Process: Neutralized (P1) is esterified at not more than 50 (preferably not more than 35) degreesC, using the concentrated sulfuric acid catalyst at 0.5-17 wt. % and (II) at 15-200% (both based on the (III)/(I) mixture), under intensive stirring to provide the maximum possible turbulence, for 0.5-3 hours. After the treatment with alkali metal hydroxide, (I) is supplied to the washing process of a biodiesel plant.

A mixture (100 g) of 65% rape oil fatty acid, 26% rape oil methyl ester and 9% methanol was treated with 70 g methanol and 11.3 g concentrated sulfuric acid, stirred intensively for 2 hours at 30 degreesC and left to stand, giving 108 g

of a phase (P2) containing 99.3 g rape oil methyl ester, 0.7 rape oil fatty acid and 8 g methanol and 73.3 g of a phase (P3) containing 11.0 g sulfuric acid, 58.3 g methanol and 4 g water of reaction. (P1) was stirred for 2 minutes with 0.35 g of 50% potassium hydroxide solution then left to stand, giving 5 g of heavy phase (containing rape oil fatty acid potassium salt, methanol and water) and 103 g of a light ester phase, which was washed successively with water and dilute sulfuric acid and concentrated to give rape oil fatty acid methyl ester, containing less than 0.2 % free fatty acids and suitable for use as diesel fuel substitute. Phase (P3) was added under stirring to 300 g of a glycerol phase (P1), obtained by potassium hydroxide-catalyzed transesterification of rape oil with methanol and containing 73 g rape oil fatty acid potassium salt, 26 g rape oil methyl ester, 100 g glycerol, 56 g methanol and 45 g water. The neutralized mixture was filtered to recover solid potassium sulfate, and separated into a light phase containing 65 g rape oil fatty acid, 26 g rape oil methyl ester and 9 g methanol and 246 g of a heavy phase containing glycerol, methanol and water, which was concentrated to give crude (at least 60%) glycerol.

TITLE-TERMS: FATTY ACID ESTER PRODUCE DIESEL FUEL SUBSTITUTE  
CONCENTRATE

SULPHURIC CATALYST ESTERIFICATION GLYCEROL PHASE OBTAIN  
PRODUCT  
TRANSESTERIFICATION

DERWENT-CLASS: D23 E17 H06

CPI-CODES: D10-B02; E10-G02E; E11-F06; H06-B04; N04-C; N07-D07;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

M423 M720 N209 N241 N262 N309 N341 N442 N512 N513

Q271 Q419

Specific Compounds

RA29MQ

Registry Numbers

309501

Chemical Indexing M3 \*02\*

Fragmentation Code

H714 H721 J0 J011 J2 J271 M210 M211 M212 M213  
M214 M215 M216 M220 M221 M222 M223 M224 M225 M226  
M231 M232 M233 M262 M272 M281 M320 M416 M620 M720  
N209 N241 N262 N309 N341 N442 N512 N513 Q271 Q419

Markush Compounds

006741001

Chemical Indexing M3 \*03\*

Fragmentation Code

C101 C108 C316 C540 C730 C800 C801 C802 C804 C805  
M411 M730 Q421

Specific Compounds

R01714 R07673

Registry Numbers

7

Chemical Indexing M3 \*04\*

Fragmentation Code

H4 H401 H481 H8 M210 M211 M272 M281 M320 M416  
M620 M730

Specific Compounds

R00270

Registry Numbers

15

Chemical Indexing M3 \*05\*

Fragmentation Code

M730

Specific Compounds

RA06I0

Registry Numbers

105392

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0270U; 0270S ; 1714U ; 1714S

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